Development of Multifunctional Catalysts for Electrooxidation of Organic Fuels

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This article reports on comprehensive studies of electrooxidation of methyl formate at different catalysts. The influence of the nanostructured palladium on the catalytic properties of platinum and platinum-ruthenium commercial nanoparticles towards electrooxidation of methyl formate is studied. All results are related to the electrooxidation process of formic acid and methanol at the same catalysts.

Introduction

Among organic compounds methanol and formic acid are considered as the most promising for fuel cell applications, although the overpotential which appears during their electrooxidation remains a serious problem. The overpotential appears as a result of strongly adsorbed by-products on the catalyst surface, mainly carbon monoxide (1-3). Despite the similar reason of the appearing overpotential, electrooxidation of methanol and formic acid proceeds with completely different mechanism. In the case of the former, formation of carbon monoxide is a step of electrooxidation process, while in the latter CO is formed as a result of non-electrochemical dehydration of the formic acid molecule.

Methyl formate is a volatile ester with boiling point 31.5 ºC and its molecule is a model connection of methanol and formic acid. It has several potential advantages as a fuel for fuel cell applications: it is less toxic than methanol and despite the presence of two carbon atoms in its molecule there is no carbon-carbon bond which presence is recognized as a main reason for low efficiency of the electrooxidation process of ethanol (4,5). The total electrooxidation of the one molecule yields 8 electrons. Since molecule of the methyl formate consists both of the methanolic and formate part, the electrooxidation process of the ester presents interesting problem and requires different electrocatalytic approaches. Electrooxidation of methanol has been extensively studied during the last years (6-10) and the PtRu binary catalytic system is now recognized as the most efficient electrocatalyst in this process (11-17). This phenomenon is explained according to the so called bifunctional mechanism (18,19): platinum shows reactivity towards C-H bonds breaking and ruthenium is expected to activate water molecules and supply -OH groups which interact with adsorbed CO.

In the electrooxidation process of formic acid, carbon monoxide cannot be formed during electrochemical step because of the same oxidation state of carbon atoms in both molecules. Despite this fact carbon monoxide appears during electrooxidation of formic acid during dehydration process and has an effect on poisoning platinum surface. It was reported that the PtPd catalyst is a particularly active system towards electrooxidation of...
formic acid (20,21). This phenomenon may be explained according to the dual path mechanism: palladium favors the direct electrooxidation of formic acid to CO$_2$ without formation of CO (22,23) The previous investigation of the electrooxidation process of the methyl formate revealed that formate part is oxidized more rapidly than methanolic one and as a result methanol was generated (24). More recently performed investigations showed that methanolic part may also contribute to the overall process but only at potentials higher than 0.4V (25). During our previous investigations we have found that combination of different active centers i.e. platinum, ruthenium and palladium supported onto tungsten oxide matrix presents active catalyst towards electrooxidation of methyl formate. PtRu system was expected to be very active both in electrooxidation of methanol and formic acid, because of the resistance for CO poisoning and the presence of nanostructured palladium was expected to promote direct electrooxidation of formate part. But even application of such complex system could not increase electrooxidation of the methanolic part sufficiently, due to the different kinetics for these processes the non-uniform electrooxidation of both parts of the ester molecule remained the main problem during electrooxidation of methyl formate (26).

In the present work we have focused on development of the multi-component catalyst based on the three active centers: platinum, ruthenium and palladium: we have performed comprehensive studies on the influence of each component on the electrooxidation process of the methyl formate and related this results to the electrooxidation of formic acid and methanol separately on the same catalysts. To achieve this we have used commercial platinum and platinum-ruthenium nanoparticles which were subsequent modified by the spontaneous adsorbed palladium. Following this conception we have used the method described by Wieckowski (27) to introduce the palladium islands in the nanostructured platinum and platinum-ruthenium layers. Such approach allowed as to fabricate four different catalytic systems: (Pt, Pt/Pd, PtRu, PtRu/Pd) and examined their activity towards electrooxidation of methyl formate, formic acid and methanol.

Experimental

All chemicals were commercial materials of analytical grade purity and were used without further purification. Solutions were prepared using doubly-distilled and subsequently de-ionized (Millipore Milli-Q) water. Argon was used to de-aerate the solutions and to keep air-free atmosphere over the solution during the measurements. All experiments were performed at room temperature (ca. 20 °C). All electrochemical measurements were performed using CH Instruments 660B or 600B workstations. The reference electrode was K$_2$SO$_4$-saturated Hg/Hg$_2$SO$_4$ while the carbon rod served as a counter electrode. The Pt and Pt/Ru inks were prepared as follows: to 5.5 mg commercial Alfa Aesar nanoparticles were added 400 μl of ethanol and 80 μl of Nafion following by stirring. The working electrode was prepared by uniform distribution of Pt or Pt/Ru ink on glassy carbon substrate. The Pt-Pd and Pt/Ru-Pd systems were fabricated by immersing Pt or Pt/Ru electrode into 10 mM Pd(NO$_3$)$_2$ + 0.5M H$_2$SO$_4$ solution. After 10 minutes electrode was rinsed with distilled water and annealed in 0.5 M H$_2$SO$_4$ by cyclization. The described procedure was repeated four times.
Results and discussion

Fig. 2 illustrates the cyclic voltammetry characteristic of Pt-Pd and PtRu-Pd catalysts. Modification of platinum with palladium ultra thin layer results mainly in the changes of the electrochemical characteristic in the hydrogen adsorption region. The peaks characteristic for hydrogen adsorption/desorption are going to overlap each other during the modification process and finally after deposition of four monolayers of palladium only one peak is visible. It should be noted that palladium deposited on the platinum layer does not show typical response for this metal. The hydrogen peaks are even smaller after palladium deposition than for the bare platinum nanoparticles. Such behavior is quite unusual taking into consideration ability of palladium for hydrogen absorption. Such features may be explained by very small thickness of the palladium which presents different properties than thicker layers. Also it should be remembered that in case of very thin layers, properties of the metal are determined by properties of the substrate on which it is deposited. Deposition of the palladium onto PtRu system also leads to the some changes in the hydrogen desorption region, however more pronounced differences appear in the “double layer” region (Fig. 1B).

Figure 1. Cyclic voltammetric responses of (A) Pt; (B) Pt-Ru catalytic systems together with (dashed lines) and without (solid lines) of adsorbed Pd. Electrolyte: 0.5 mol dm$^{-3}$ H$_2$SO$_4$. Scan rate: 50 mV s$^{-1}$.

Electrochemical measurements performed in the presence of methyl formate at four different catalysts (Pt, Pt/Pd, PtRu and PtRu/Pd) indicate strong differences between examined systems (Fig. 2). For the catalysts containing palladium electrooxidation process starts very rapidly and reach almost double current when compare to the system without palladium. This feature is particular visible for the platinum nanoparticles in the reverse scan. But what is more important, both in the case of platinum and platinum-ruthenium system, modification of the catalytic surface with palladium leads also to the higher activity at lower potentials. Parallel experiments performed at identical catalytic systems in the presence of formic acid allow to conclude that activating role of palladium may be ascribed mainly to the activation of the systems towards electrooxidation of the
formate part of the ester molecule. Results registered for the electrochemical oxidation of formic acid show very similar course to the cyclic voltammograms registered for the electrooxidation of methyl formate. The main difference between registered measurements is more pronounced activating effect of the palladium at low potential region in the case of formic acid electrooxidation (Fig. 3). This results are coherent with the previous investigations described briefly in the introduction part: in the presence of H\textsuperscript{+} the ester molecule yields hydrolysis into formate and methanolic parts and faster electrooxidation of the formate part results in the generation of carbon dioxide and methanol as a main products.

Figure 2. Voltammetric oxidation of 0.5 mol dm\textsuperscript{-3} methyl formate at (A) Pt; (B) Pt-Ru catalytic systems together with (dashed lines) and without (solid lines) of adsorbed palladium. Electrolyte: 0.5 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4}. Scan rate: 50 mV s\textsuperscript{-1}.

Figure 3. Voltammetric oxidation of 0.5 mol dm\textsuperscript{-3} formic acid at (A) Pt and (B) Pt-Ru catalytic systems together with (dashed lines) and without (solid lines) of adsorbed palladium. Electrolyte: 0.5 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4}. Scan rate: 50 mV s\textsuperscript{-1}.
To get a complete data of the ability of the methyl formate to yield electrooxidation the effect of the palladium modification on the electrooxidation of methanol was also studied. Introducing of the palladium layer resulted in the deactivation of the platinum and platinum-ruthenium catalysts. This deactivation is unnoticeable in the low potential range (0 – 0.35V) but since 0.4V it starts to play a significant role and particularly in the case of the platinum system we can observe strong suppression of the catalytic current for the system containing palladium (Fig. 4).

Figure 4. Voltammetric oxidation of 0.5 mol dm$^{-3}$ methanol at (A) Pt and (B) Pt-Ru catalytic systems together with (dashed lines) and without (solid lines) of adsorbed palladium. Electrolyte: 0.5 mol dm$^{-3}$ H$_2$SO$_4$. Scan rate: 50 mV s$^{-1}$.

In opposite to the ruthenium, palladium does not act as a –OH source, its activating role is rather to influence the surface reactions by geometric effect. This feature explains why palladium has a strong activating effect on electrooxidation of formic acid. Presence of palladium enables the oxidation of this compound via dehydrogenation path (direct path) instead of dehydration path. In the case of electrooxidation of methanol process carbon monoxide is formed on the electrochemical way and is impossible to avoid formation of this compound, thus more important is a presence of ruthenium as a source of –OH groups.

This results were confirmed also by chronoamperometric measurements (not shown here). Activating role of the palladium in the electrooxidation of methyl formate process was observed under different (0.3V, 0.4V and 0.5V) potentials.

To get more insight into the mechanism of the studied processes cyclic voltammetry measurements for different combination of investigated electrolytes have been performed (Fig. 5). Addition of formic acid or methanol to the methyl formate solution moves the equilibrium of the hydrolysis process towards formation of the substrate. As a result, in the solution is mainly ester and formic acid or methanol respectively. In the solution
containing equal amounts of the formic acid and methyl formate proceeds mainly electrooxidation of the first one (Fig. 5). The value of the current registered in that case is the highest. In the solution containing 0.25 mol dm\(^{-3}\) of methanol in the presence of 0.25 mol dm\(^{-3}\) methyl formate we can observe the decrease of the current value when compare to the measurements registered in the 0.5 mol dm\(^{-3}\) solution of the pure ester. Stoppage of the hydrolysis of methyl formate in the solution results in the increasing efficiency of the transport non-dissociated molecules to the catalyst surface.

Figure 5. Influence of the addition of formic acid and methanol on the electrooxidation process of methyl formate observed at four different catalysts: Pt (A), Pt/Pd (B), PtRu (C), PtRu/Pd (D). Solid lines: 0.5 mol dm\(^{-3}\) methyl formate, dashed lines: 0.25 mol dm\(^{-3}\) methyl formate + 0.25 mol dm\(^{-3}\) formic acid, dotted lines: 0.25 mol dm\(^{-3}\) methyl formate + 0.25 mol dm\(^{-3}\) methanol.
As the result of non-uniform electrooxidation of both parts of molecule in the space at electrode surface methanol is generated, which is also additionally supplied from the solution. This process effects in decreasing of the efficiency of methyl formate electrooxidation. This effect is negligible in the range of more negative value of the applied potential what is even more pronounced under chronoamperometric conditions. Addition of the methanol does not have significant effect on the value of the catalytic current in this potential range (an exception is the Pt-Ru system, in that case increasing of the catalytic current was observed). The lack of the formic acid in the solution results in decreasing of the catalytic current what is especially visible on the voltammograms registered for the systems modified with palladium.

Conclusions

Modification of Pt and Pt-Ru nanoparticles with ultra-thin films of palladium results in the enhancement of their electrocatalytic properties towards electrooxidation both methyl formate and formic acid as demonstrated in terms of increases of the respective voltammetric and amperometric catalytic currents. The activation by palladium is the most effective in a case of formic acid electrooxidation at platinum nanoparticles. The platinum activation mechanism by palladium is well known and well documented in the literature. Electrooxidation of methyl formate is a complex process in which two carbon atoms on different oxidation states have to be oxidized. The combination of three different active centers: platinum, palladium and ruthenium was an attempt to improve overall electrooxidation process of ester molecule but due to the huge difference in the kinetic of electrooxidation of two parts of the molecule mainly formate part is oxidized and the combination of Pt, Ru and Pd allows to make the oxidation process only slightly more uniform than on the bimetallic catalyst.

References